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Electrical resistivity in the $Fe_{100-x}B_x$ series ($13 \leq x \leq 26$)

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The electrical resistivity of the $Fe_{100-x}B_x$ series ($13 \leq x \leq 26$) has been measured in the temperature range of $80 \leq T \leq 300$ K. The temperature coefficient of resistivity α and plots of the percentage change of resistivity $\Delta\rho/\rho$ in this temperature range versus x show an abrupt fall from $x=13$ to $x=16$ and then they are nearly independent of concentration for $16 \leq x \leq 26$. Negligible sample-to-sample variation of α (for the same x) indicates excellent homogeneity of the alloys. An order-of-magnitude calculation is given for α and $\Delta\rho/\rho$ for the first time in this Fe-B series and it agrees reasonably well with our experimental data. A physical explanation of its behavior is offered in terms of the structure factor and stability of this amorphous series. A comment is made on the applicability of Ziman's theory in the present case.

I. INTRODUCTION

The subject of the present investigation is the electrical resistivity in metallic glasses. The electrical resistivity of a typical metallic glass differs from that of a typical crystalline metal in many ways, e.g.,

(i) In metallic glasses, scattering from structural disorder is the dominant mechanism reponsible for resistivity and hence they have a much higher residual resistivity as compared to the crystalline materials.

(ii) The temperature coefficient of resistivity α of metallic glasses is much smaller than that of the corresponding crystalline materials and can be both positive as well as negative.

Recently, this has been a subject of wide interest and experimental studies of electrical transport properties and theoretical predictions on the temperature dependence of resistivity have also been made. In the present investigation of electrical resistivity we have chosen $Fe_{100-x}B_x$ series with $13 \leq x \leq 26$ manufactured by Allied Chemical Corp. Similar resistivity measurements on $Fe_{100-x}B_x$ series with $15 \leq x \leq 22$ were reported by Mogro-Campero and Walter.[1] Their samples were made by General Electric. The results of their studies could be summarized as follows.

(i) The greatest experimental uncertainty in the resistivity versus temperature measurement arose from sample-to-sample variation. When cycled in the temperature range between 20 and 300 K, each sample gave a reproducible value of resistivity ρ, but a sample-to-sample spread of $\sim 1\%$ occurred in ρ at low temperatures. The final experimental uncertainties $\Delta\alpha$ in the value of the slope α of ρ vs T curve, in their measurements, had a range of $(0.03-0.20)\times 10^{-4}$ K^{-1}, where α was typically 1.5×10^{-4} K^{-1}.

(ii) Their samples showed a linear temperature dependence of resistivity in the interval $120 \leq T \leq 300$ K and a T^2 dependence in the range $20 \leq T \leq 100$ K.

(iii) The temperature coefficient of resistivity $\alpha=(1/\rho)_{\mathrm{RT}}(\partial\rho_T/\partial T)$ was positive over the entire range $15 \leq x \leq 22$, and approximately constant as a function of x.

Mogro-Campero[2] had tried to calculate the Debye temperature Θ_D with the help of existing theories and found that for the Fe-B series $\Theta_D \simeq 370$ K.

The motivations behind the present work are (i) to minimize the error $\Delta\alpha$ through more precise as well as repeated measurements and (ii) to do the experiment over a wider range of composition, to see if there is any trend in the α vs x graph. From our experimental data of resistivity ρ vs T($80 \leq T \leq 300$ K) in Fe-B binary series, we have tried to find out the following: (i) the sign of α as well as its concentration (x) dependence in the wider range $13 \leq x \leq 26$, (ii) the percentage change of resistivity, $\Delta\rho/\rho$ from 300 to 80 K as a fuction of x, and (iii) approximate Debye temperature Θ_D.

We have also tried to do for the first time in this Fe-B series an order-of-magnitude calculation for α and $\Delta\rho/\rho$ with the help of existing theories and have compared them with our data. An attempt will be made to physically explain their behavior in terms of the structure and stability of this amorphous series.

II. THEORY

If one takes the view that amorphous metallic alloys are frozen liquids, one can apply Ziman's theory of liquid metals to understand the temperature dependence of resistivity in metallic glasses. Using the concept of the above theory, various authors[3] had explained the temperature dependence of resistivity in many amorphous systems. In Ziman's theory of liquid metals the temperature dependence of resistivity is included by taking into account the change in structure factor $S(k)$ as T is varied. In metallic glasses one should properly take care of resistivity change due to electron-phonon scattering. The first peak height of $S(k)$ versus the wave-vector k graph decreases with increasing temperature, giving rise to a negative α whereas the number of phonons increases with temperature, resulting in a positive α. Both these mechanisms are competitive. The final sign of α is determined by the dominant one.

Following Nagel,[3] the electrical resistivity ρ of a metallic glass is given by

$$\rho = \frac{30\pi^3\hbar^3}{me^2k_f^2E_F\Omega}\sin^2[\eta_2(E_F)] \times \{1+[S_T(2k_F)-1]e^{-2[W(T)-W(0)]}\} , \quad (1)$$

where k_F is the Fermi wave vector, Ω is the atomic volume, $W(T)$ is the Debye-Waller factor at a temperature T, $\eta_2(E_F)$ is the $1=2$ partial-wave phase shift at the Fermi energy E_F, $S_T(2k_F)$ is the structure factor corresponding to $k=2k_F$, and $\hbar$, m, and e have their usual meaning.

Also,

$$\alpha = \frac{1}{\rho_{\text{RT}}}\frac{\partial \rho_T}{\partial T} \simeq \frac{2[1-S_T(2k_F)]}{S_T(2k_F)}\frac{\partial W(T)}{\partial T} . \quad (2)$$

Since $\partial W(T)/\partial T > 0$, α is negative only if $S_T(2k_F) > 1$, i.e., if $2k_F$ is near k_P, the position of the first peak in the $S(k)$ vs k graph, then a negative temperature coefficient is expected. Now coming back to Eq. (2), the asymptotic temperature dependence of $W(T)$ in the Debye approximation is given by

$$W(T) = \begin{cases} W(0)+4W(0)\frac{1}{6}\pi^2(T/\Theta_D)^2, & T << \Theta_D \quad (3) \\ W(0)+4W(0)(T/\Theta_D), & T \geq \Theta_D \quad (4) \end{cases}$$

where

$$W(0) = \frac{3}{8}\frac{\hbar^2k^2}{Mk_B\Theta_D} \quad (5)$$

and M is the atomic weight.

Thus an estimate of α could be made for individual alloys, from Eqs. (2) and (4), if the structure factor $S(k)$ at the corresponding $2k_F$ value (which depends on the number of conduction electrons per unit volume) and Θ_D are known. The percentage change of resistivity $\Delta\rho/\rho$ from 300 to 80 K is given by

$$\frac{\Delta\rho}{\rho} = \frac{\rho(300\text{ K})-\rho(80\text{ K})}{\rho(80\text{ K})} = -\frac{C[S_T(2k_F)-1]}{S_T(2k_F)} . \quad (6)$$

This expression along with the constant C could be easily derived from Eqs. (1), (3), and (4). Using the same equations Θ_D is found to be

$$\Theta_D = \frac{\pi^2}{6}\frac{\alpha}{s} , \quad (7)$$

where

$$s = \frac{\partial\rho}{\rho_{\text{RT}}\partial(T^2)} \quad \text{for } T << \Theta_D .$$

III. EXPERIMENTAL PROCEDURE

The samples were in the form of thin ribbons, typically 1 mm wide and 30 μm thick, and were cut to ~15 mm length for resistivity measurements. The sample holder consisted of a cylindrical copper block machined to provide a plane rectangular surface, which gives a good thermal contact with the sample mounted on it. This block was electrically insulated from the sample by coating it with a thin layer of araldite. The sample was free to expand on this layer of araldite. The four probes were neatly soldered with special low-melting-point Cerroseal-35 solder to prevent excessive heating of the sample. A copper-constantan thermocouple was adhered to the copper block for measuring the temperature of the heat sink and hence that of the sample. The thermocouple voltage was directly read on a Keithley digital multimeter (Model 179) giving a temperature correct to within $\frac{1}{3}$ K. In the four-probe resistivity measurement setup, a current of ~ 100 mA was passed through the sample from a Hewlett-Packard power supply (Model 6177 C). At room temperature the sample voltage (typically ~ 100 mV) was compensated by adjusting a Leeds and Northrup K-3 potentiometer put in series opposition and using a digital voltmeter (Keithley Model 174, sensitivity $\simeq 0.1\ \mu\mathrm{V}$) as a null detector. As the sample was cooled the change in resistivity was directly read on the digital voltmeter and thermocouple voltage was simultaneously recorded. The heating data was also taken in a similar manner. Thus a resistance change of a few parts in 10^6 could be detected in the present setup.

IV. RESULTS

The behavior of electrical resistivity as a function of temperature is the same in all the samples. In Fig. 1 we have plotted the ratio of resistivity at any temperature T and that at room temperature $\rho_T/\rho_{\mathrm{RT}}$ against T in the temperature range $80 \le T \le 300$ K for some of these metallic glasses. The resistivity shows a departure from linearity below about 150 K. In both the heating and cooling cycles measurements were repeated at least 2—3 times for each sample. Different pieces of the same composition were also measured in a few cases to check for the inaccuracy arising from sample-to-sample variation. The temperature coefficient of resistivity α (high-temperature slope of the $\rho_T/\rho_{\mathrm{RT}}$ vs T graph) is positive over the entire range of x and is reproducible within the error limits. The percentage change of resistivity $\Delta\rho/\rho$ in the above temperature range can be found directly from Fig. 1. Figure 2 shows a $\rho_I/\rho_{\mathrm{RT}}$ vs T^2 plot for all six samples in the temperature range $80 \le T \le 130$ K. The slopes of these curves and the corresponding α are used to calculate Θ_D.

In Table I we have listed the composition, crystallization temperature T_{cr}, as well at $\Delta\rho/\rho$, α, and Θ_D for all the alloys. It is to be noted that the dimensional change of the sample due to thermal expansion contributes about 6% to the values of α

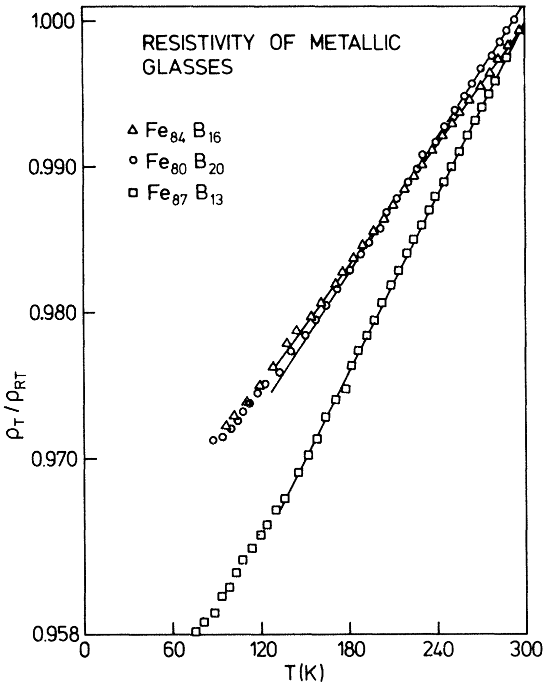

FIG. 1. Ratio of resistivity at any temperature T and that at room temperature $\rho_T/\rho_{\mathrm{RT}}$, vs T in the temperature range $80 \le T \le 300$ K for some Fe-B metallic glasses.

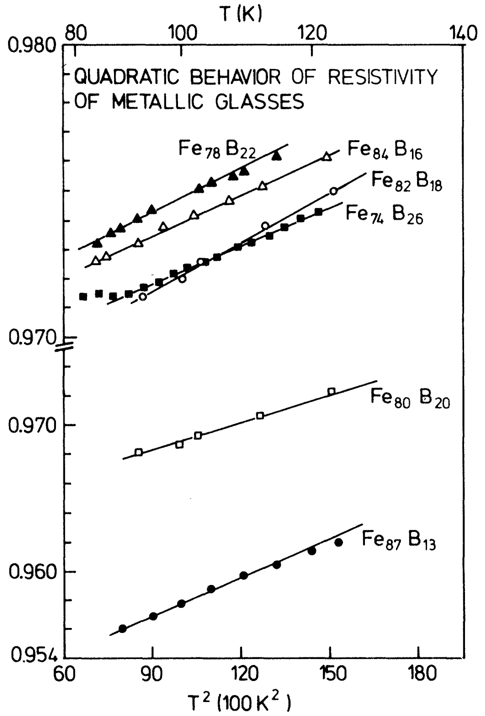

FIG. 2. Ratio of resistivity at any temperature T and that at room temperature $\rho_I/\rho_{\mathrm{RT}}$ vs T^2 to show the quadratic behavior of resistivity at lower temperatures for Fe-B metallic glasses.

TABLE I. Values of T_{cr}, $\Delta\rho/\rho$, α, and Θ_D in $\mathrm{Fe}_{100-x}\mathrm{B}_x$ ($13 \leq x \leq 26$) series in the temperature range $80 \leq T \leq 300$ K.

Composition	T_{cr} (K)	$\frac{\Delta\rho}{\rho}$ (%)	α (10^{-4} K^{-1})	Θ_D (K)
$\mathrm{Fe}_{87}\mathrm{B}_{13}$	586	4.9	2.43 ± 0.07	555 ± 90
$\mathrm{Fe}_{84}\mathrm{B}_{16}$	643	2.8	1.53 ± 0.15	520 ± 90
$\mathrm{Fe}_{82}\mathrm{B}_{18}$	660	3.0	1.49 ± 0.01	390 ± 50
$\mathrm{Fe}_{80}\mathrm{B}_{20}$	660	3.3	1.62 ± 0.04	400 ± 50
$\mathrm{Fe}_{78}\mathrm{B}_{22}$	666	2.8	1.49 ± 0.06	380 ± 50
$\mathrm{Fe}_{74}\mathrm{B}_{26}$	688	3.0	1.40 ± 0.04	520 ± 90

given in Table I.

Figure 3 shows the boron concentration, x, dependence of α and $\Delta\rho/\rho$. Both these curves show an abrupt fall in going from $x = 13$ to $x = 16$ and then they are more of less independent of x for $16 \leq x \leq 26$.

V. DISCUSSION

The error bars of α given in Table I, include errors coming from (a) repeated measurements on a given piece of alloy and (b) measurements on different samples of the same composition. The average value of $\Delta\alpha$ over the entire composition range is (except for $x = 16$) $\simeq 0.05 \times 10^{-4}$ K^{-1}, which is less than half of the average error ($\pm 0.12 \times 10^{-4}$ K^{-1}) found by Mogro-Campero and Walter.[1] As mentioned in Sec. I these authors found that $\Delta\alpha$ was mainly due to the sample-to-sample variation of α. In contrast to this we find that $\Delta\alpha$ due to this variation is not more than 0.05×10^{-4} K^{-1}. As a matter of fact, in $\mathrm{Fe}_{84}\mathrm{B}_{16}$ alloy we could exactly reproduce the result in two different peices. This might imply that our samples are more homogeneous.

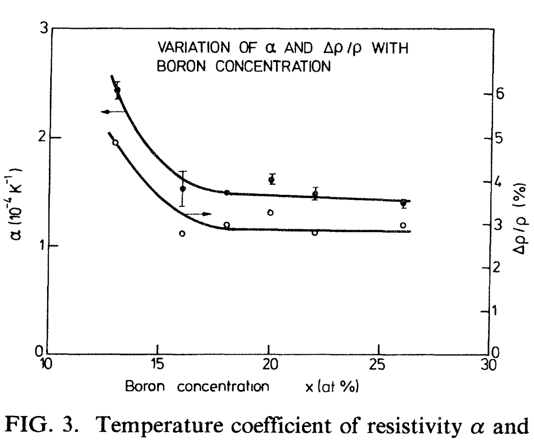

FIG. 3. Temperature coefficient of resistivity α and the percentage change of resistivity $\Delta\rho/\rho$ (see text for definitions) vs x, the concentration of boron for Fe-B metallic glasses.

In the Fe-B series the sign of α is positive. As shown in Sec. II [Eq. (2)], α is expected to be positive only for materials with the structure factor $S_T(2k_F) < 1$. The value of k_F is determined in the free-electron model, from n, the number of conduction electrons per unit volume as

$$k_F = (3\pi^2 n)^{1/3} . \tag{8}$$

One could calculate k_F for the Fe-B series in the following way: For Fe we have taken[4] $n_{\mathrm{Fe}} \simeq 2 \times 10^{28}\mathrm{m}^{-3}$, atomic weight = 56, and density = 7.8 g/cm^3; with these data Z_{Fe} is easily calculated to be $\simeq 0.24$, where Z is the effective number of conduction electrons per atom. Further, using atomic weight of $B = 10$, density of the particular metallic glass, say $\mathrm{Fe}_{80}\mathrm{B}_{20} = 7.4$ g/cm^3 and $Z_B = 1.6$,[4] we have calculated n for $\mathrm{Fe}_{80}\mathrm{B}_{20}$ as $= 4.75 \times 10^{28}\mathrm{m}^{-3}$. Hence, from Eq. (8), k_F is found to be $\simeq 1.1 \times 10^{10}\mathrm{m}^{-1}$. The corresponding $S_T(k)$ value (for $2k_F = 2.2 \times 10^{10}\mathrm{m}^{-1}$) is found to be $\simeq 0.15$ from the $S_T(k)$ vs k graph.[5] For the entire series $2k_F$ value lies between 2.0×10^{10} and 2.3×10^{10} m^{-1} and $S_T(2k_F)$ increases monotonically with $2k_F$. Although precise estimation of $S_T(k)$ is extremely difficult from this graph, they are definitely much less than 1 and hence the values of α for the entire series have to be positive. An order-of-magnitude calculation of α for $\mathrm{Fe}_{80}\mathrm{B}_{20}$ is made by using Eqs. (2) and (4) and taking $M \simeq 50$ and $\Theta_D = 400$ K. Finally α comes out to be $\simeq 1.4 \times 10^{-4}$ K^{-1}, which is in good agreement with our experimental α ($\sim 1.6 \times 10^{-4}$ K^{-1}).

The variation of α with x is shown in Fig. 3. The temperature coefficient of resistivity falls abruptly from $x = 13$ to $x = 16$, and in the range $16 \leq x \leq 26$, α is almost independent of concentration. The latter is in agreement with the results of Mogro-Campero and Walter.[1] In fact, the concentration dependence of α comes from two factors, namely, the structure factor term and the Debye-Waller factor [see, for example, Eq. (2)]. As x increases, the $2k_F$ value and hence $S_T(2k_F)$ increases monotonically, as mentioned above. Thus the positive α should decrease with x, if $S_T(2k_F)$ was the only factor governing it. But α depends on the Debye-Waller factor too. The x dependence of $\partial W(T)/\partial T$ mainly comes from the x dependence of $W(0)$ and this increases with x. Thus qualitatively it may be argued that the decreasing effect on α from $S_T(2k_F)$ and the increasing effect on it from $\partial W(T)/\partial T$ are competitive and hence in the range $16 \leq x \leq 26$, α becomes approximately independent of concentration. Such type of variation of α with x might be correlated with the variation of the crystallization temperature T_{cr} of these alloys with x, as studied by Hasegawa and Ray.[6] They found that T_{cr} abruptly increases from $x=13$ to $x=16$, and then there is a constant region in the range $18 \leq x \leq 22$ and after that it slowly increases with x. Such a correlation gives rise to a stability criterion also in terms of α. One should note that the effect of magnetic scattering, which might give an additional positive contribution to α, is ignored here.

In the temperature range $80 \leq T \leq 300$ K, $\Delta\rho/\rho$ is calculated from Eq. (6) by evaluating C and using the values of Θ_D, M, and k_F for $Fe_{80}B_{20}$. It is found that $\Delta\rho/\rho \simeq 4.2\%$. As shown in Fig. 3, $\Delta\rho/\rho$ in the temperature range $80 \leq T \leq 300$ K is independent of concentration in the range $16 \leq x \leq 26$, with values lying between 2.8 and 3.3%. However, for $x=13$ this percentage change is higher, viz., 4.9%.

Now finally we come to the discussion of the electronic stability criterion. According to Nagel and Tauc,[7] for stable alloys the effective number of conduction electrons per atom $z_{\rm eff}$ corresponding to $2k_F=k_P$ should be around 1.7. For the present $Fe_{100-x}B_x$ series

$$Z_{\rm eff}=Z_{\rm Fe}(1-x)+Z_{\rm B}x \ . \tag{9}$$

According to them, $Z_{\rm Fe}=1$ and $Z_{\rm B}=3$ (valency of B). This gives a stability around $x=35$, which is far away from the stable region of this series (which is around $x \simeq 20$). We have calculated the $Z_{\rm eff}$ at k_P for this particular series. Using $k_P=3\times10^{10}$ m^{-1},[5] it can be easily shown that $Z_{\rm eff}$ corresponding to the peak of the $S_T(k)$ vs k graph of the Fe-B series is $\simeq 1.2$ electrons per atom. The $Z_{\rm eff}$ values for this series of stable alloys lie between 0.4 and 0.6 [calculated from Eq. (9) using $Z_{\rm Fe}=0.24$ and $Z_{\rm B}=1.6$ (Ref. 4)] and hence they are obviously far away from 1.2. Thus we find that one could still have stable alloys with $2k_F << k_P$. This conclusion is also corroborated by the interpretation that we have given to justify the positive α for the Fe-B series. Since $0.4 \leq Z_{\rm eff} \leq 0.6$ is much less than the $Z_{\rm eff}$ corresponding to the peak of the $S_T(k)$ vs k graph, we get $S_T(k) << 1$, giving rise to a positive α. Also, taking these values of $Z_{\rm eff}$ in our theoretical calculations, we could reproduce all our experimental data, within reasonable limits. So, one could say that the stability criterion set up by Nagel and Tauc is not applicable to the stable amorphous alloys with positive α, although the criterion holds quite well with those having negative α.

The Debye temperature of all six samples were calculated from Eq. (7). The Θ_D values for $18 \leq x \leq 22$ are 390 ± 50 K (similar to those found by Mogro-Campero[2]), but for $x=16$ and 13 it shows higher values of 540 ± 90 K, and for $x=26$ again it is around 520 K (exact values are given in Table I). The uncertainty in s introduces large error bars in Θ_D values. Onn *et al.*[8] had found from heat-capacity measurements in $Fe_xNi_{80-x}P_{14}B_6$ metallic glasses that Θ_D is invariably lower in the amorphous alloys as compared to their nearest available crystalline counterparts. We are unable to understand why we find for our Fe-B alloys with $x=13$, 16, and 26 that Θ_D is higher than that of pure Fe ($\simeq 420$ K). However, specific-heat measurements in this series of alloys could certainly establish more accurately the Debye temperatures.

Lastly, a comment is due on the applicability of Ziman's theory in these metallic glasses. From Eqs. (1), (3), and (4), one can easily find that

$$\rho(T)=\begin{cases} a\pi^2T^2/6\Theta_D^3 & \text{for } T << \Theta_D & (10)\\ aT/\Theta_D^2 & \text{for } T \geq \Theta_D \ . & (11)\end{cases}$$

Equation (11) clearly shows that the variation of $\rho(T)$ with T should deviate from linearity for temperatures below Θ_D. In contrast to this, we find that the $\rho_T/\rho_{\rm RT}$ vs T graph (see Fig. 1) is linear down to temperatures much less than Θ_D, e.g., in $Fe_{80}B_{20}$, $\Theta_D \simeq 400$ K while $\rho(T)$ deviates from linearity only below $\simeq 160$ K. Unfortunately no one seems to have pointed this out recently for the Fe-B series. Esposito *et al.*[9] had shown that in the strong scattering liquids (Fe, Co) the extended Ziman theory could only give a qualitative description of the resistivity as against the weak scattering cases (Ni, Cu) where one gets a better quantitative estimate of resistivity. Thus the values of α and $\Delta\rho/\rho$, calculated here on the basis of the above theory, should be taken as only order-of-magnitude estimates.

VI. CONCLUSION

To conclude:

(i) We have been able to find experimentally the concentration dependence of the temperature coefficient of resistivity and the percentage resistivity change between 300 and 80 K in $Fe_{100-x}B_x$ metallic glasses in a wider composition range.

(ii) These quantities are also calculated for the first time in this Fe-B series using existing theories and they are in reasonable agreement with our data.

(iii) An attempt is made to correlate them in terms of the structure factor and stability of this amorphous series.

(iv) The limitation of the applicability of Ziman's theory to these amorphous alloys is also pointed out.

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